



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/08166 <b>(22) International Filing Date:</b> 14 May 1997 (14.05.97)  <b>(30) Priority Data:</b> 60/018,087                      22 May 1996 (22.05.96)                      US  <b>(71) Applicant (for all designated States except US):</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> YANG, Zhen-Yu [CN/US]; 2609 Marhill Drive, Wilmington, DE 19810 (US).  <b>(74) Agent:</b> HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROCESS USING CF <sub>2</sub> I <sub>2</sub> AND OLEFINS FOR PRODUCING DIIDO FLUOROCOMPOUNDS, AND PRODUCTS THEREOF  <b>(57) Abstract</b>  A process is disclosed for making diiodofluorinated compounds of the formula ICF <sub>2</sub> (A) <sub>n</sub> I wherein n is an integer of at least 1 and each A is CXYCQZ wherein each X, Y, Q and Z are each independently selected from the group consisting of H, F, Cl, R <sub>F</sub> and OR <sub>F</sub> , and R <sub>F</sub> is a perfluoroalkyl group or perfluorinated polyether group wherein one or more of the fluorines is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride. The process involves reacting an olefin of the formula CXY = CQZ with CF <sub>2</sub> I <sub>2</sub> at a temperature in the range of from about 120 °C to 240 °C. Diiodofluorinated compounds of the formula ICF <sub>2</sub> CH <sub>2</sub> CHR <sub>F</sub> I are also disclosed.		

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TITLEPROCESS USING  $\text{CF}_2\text{I}_2$  AND OLEFINS FOR PRODUCING DIIDO  
FLUOROCOMPOUNDS, AND PRODUCTS THEREOFFIELD OF THE INVENTION

5 This invention relates to diiodofluorinated compounds and their production, and more particularly to using  $\text{CF}_2\text{I}_2$  and olefinic compounds as reactants for producing diiodofluorinated compounds.

BACKGROUND

10 Diiodoperfluoroalkanes are useful as chain transfer reagents for fluoroelastomers and in the free radical polymerization of fluorinated vinyl monomers. See U.S. Patent Nos. 4,243,770 and 4,361,678. The reaction of  $\text{CF}_2\text{I}_2$  with olefins allows the stepwise addition to the chain, thereby providing controlled chain growth. The production of these diiodoperfluoroalkanes at relatively high yields has been hampered in the past by the lack of a method by  
15 which to produce relatively high yield and purity  $\text{CF}_2\text{I}_2$ . However, as described in commonly held U.S. Patent Application No. 60/012,160, filed February 23, 1996,  $\text{CF}_2\text{I}_2$  can be produced in sufficiently high yields to facilitate the reactions described below.

Commonly held U.S. Patent No. 5,504,248 describes the production of  
20 diiodofluoroalkanes by reacting  $\text{I}_2$  with hexafluorocyclopropane. This process involves a relatively complex ring-opening reaction, and uses relatively expensive starting materials.

Elsheimer, et al., J. Org. Chem. 1984, 49, pp. 205-207, discloses reactions of  $\text{CF}_2\text{I}_2$  with hydrocarbon olefins to produce iododifluoroalkenes via photolysis,  
25 or diiododifluoroalkanes via reactions catalyzed by peroxide at temperatures less than  $100^\circ\text{C}$ . The use of peroxides to form the diiododifluoroalkanes could result in the production of other reaction products, which would have to be separated from the desired products, thus adding an additional step, as well as the associated costs involved with such purification.

30 Many citations are found throughout the literature describing diiodofluorinated compounds, but interest continues in developing new, efficient processes for producing selected diiodofluorinated compounds.

SUMMARY OF THE INVENTION

A process is provided for making diiodofluorinated compounds of the  
35 formula  $\text{ICF}_2(\text{A})_n\text{I}$  wherein n is an integer of at least 1 and each A is  $\text{CX}_1\text{Y}_1\text{CQ}_1\text{Z}_1$  wherein each X, Y, Q, and Z are each independently selected from the group consisting of H, F, Cl,  $\text{R}_\text{F}$  and  $\text{OR}_\text{F}$ , and  $\text{R}_\text{F}$  is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to

20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride. The process comprises  
5 reacting an olefin of the formula  $CXY=CQZ$  with  $CF_2I_2$  at a temperature in the range of from about 120°C to 240°C.

Diiodofluorinated compounds of the formula  $ICF_2CH_2CHR_FI$ , where  $R_F$  is as indicated above, are also provided in accordance with this invention.

#### DETAILED DESCRIPTION

10 This invention provides a process by which  $CF_2I_2$  is reacted with olefins to produce diiodofluorinated compounds, generally described in Equation (I) below:



15 In Equation (I), A represents  $(CXYCQZ)$ , and X, Y, Q and Z are each independently H, F, Cl,  $R_F$  or  $OR_F$ , and preferably at least one of X, Y, Q and Z is F. The number of repeat units of A, as represented by n in Equation (I) is 1 or greater and is preferably from 1 to about 5, more preferably from 1 to 3. Of note  
20 are embodiments where n is 1; embodiments where n is 2; and embodiments where n is 3.

The process represented by Equation (I) takes place at an elevated temperature. It has been found in accordance with this invention that when conducted at temperatures of about 120°C or above, the reaction needs no  
25 chemical catalyst or initiator to proceed. Indeed, the process of this invention is typically conducted in the substantial absence of a catalyst or initiator. By "substantial absence of catalyst or initiator" is meant that the reaction would effectively proceed even in the absence of any catalyst or initiator which might be added. By "catalyst or initiator" is meant materials or chemicals such as, for  
30 example, peroxides or azo compounds, which have been previously required to produce diiodofluorinated compounds at lower temperatures.

The temperature range is generally between about 120°C and about 240°C, and is preferably between about 170°C and about 190°C. The process can take place in the liquid or gas phase. Liquid phase reactions may be conducted in  
35 solution in inert solvents such as, for example, fluorocarbons, fluorochlorocarbons and hydrofluorocarbons, or (preferably) may be conducted neat. Although not necessary, if the reaction is carried out in the liquid state, moderate agitation is preferred. It is also preferred that oxygen and water are excluded from the

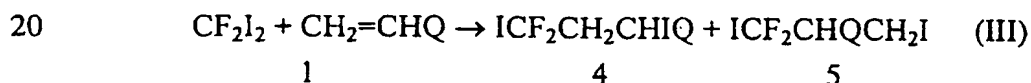
reaction, and it may be convenient to carry out the reaction under an inert gas blanket, such as nitrogen.

Pressure is not critical, autogenous pressure (of all the ingredients) being generally the convenient operation pressure. Typically, the reaction is conducted  
 5 at pressure within the range of from about 20 psi (about 138 Pa) to about 1000 psi (about 6900 Pa). Non-limiting examples of reaction vessels include shaker tubes, tanks, autoclaves and reactors.

It is noted that for each addition of olefinic starting material, the unit A can have either of two orientations, with either carbon involved with the olefinic bond,  
 10 attaching to the end carbon of the iodo reactant. Accordingly, where the carbons involved with the olefinic bond are differently substituted, the addition of each A group can result in either of two products. Thus for example, when n is 1, the reaction can be represented as:

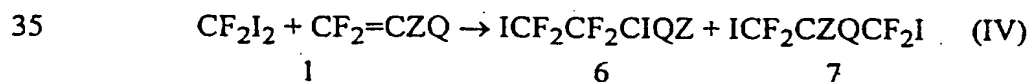


When X, Y and Z are each H in Equation (II), the reaction may be represented by Equation (III) below:



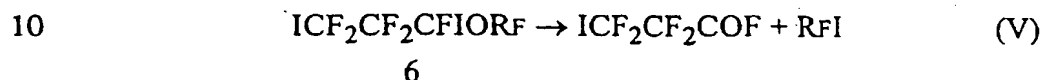
Both fluorinated or non-fluorinated olefins, as determined by the composition of Q, give relatively good yields of adducts. When reacted with ethylene, a  
 25 relatively higher yield of adduct 4 is obtained, as described in Example 1 below. A mixture of regioisomers 4 and 5 is, however, formed with propylene and vinyl fluoride (Examples 2 and 8, respectively). Fluoroalkyl substituted olefins or fluorinated polyether substituted olefin such as  $\text{CH}_2=\text{CHR}_\text{F}$  where  $\text{R}_\text{F}$  is highly fluorinated (Examples 3 and 4) also undergo an addition reaction with  $\text{CF}_2\text{I}_2$  to  
 30 give 4 exclusively. Examples of highly fluorinated  $\text{R}_\text{F}$  groups include  $\text{CF}_2\text{CF}_2\text{Br}$ ,  $\text{CF}_2\text{CF}_2\text{I}$ , and perfluoroalkyl groups (e.g.,  $\text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$  and  $\text{C}_8\text{F}_{17}$  groups).

Preferably at least one of X, Y, Z and Q is F. When X and Y are each F in Equation (I), the reaction may be represented by Equation (IV) below:

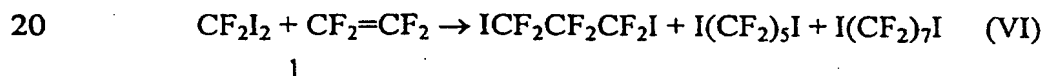


Of note are embodiments of Equation (IV) where Q is F, H,  $\text{R}_\text{F}$  or  $\text{OR}_\text{F}$  and embodiments where Z is F. Fluorinated olefins such as  $\text{CF}_2=\text{CFH}$ ,  $\text{CF}_2=\text{CFCF}_3$   
 40 and  $\text{CF}_2=\text{CH}_2$  give mixtures of regioisomers 6 and 7. Unlike other perfluoroalkyl iodides,  $\text{CF}_2\text{I}_2$  cleanly adds to perfluorovinyl ethers of the formula  $\text{CF}_2=\text{CFOR}_\text{F}$

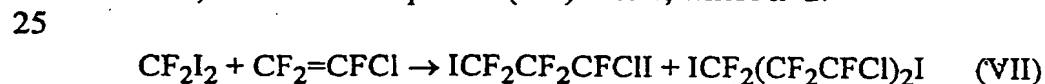
to give compound 6 ( $Q = OR_F$ ), along with small amounts of compound 7 ( $Q = OR_F$ ). The functional groups such as ester, sulfonyl fluoride and nitrile in the vinyl ethers do not interfere with the addition reaction, so that various functional diiodocompounds may be prepared, as found in Examples 12-15. When the reaction mixture of fluorovinyl ethers and  $CF_2I_2$  is subjected to prolonged heating, as in Examples 12 and 15, the initially formed compound 6, in Equation (V) below, where  $Q = OR_F$ , decomposes to  $ICF_2CF_2COF$  and  $R_FI$  (see also U.S. Patent No. 5,504,248).



The addition of  $R_FI$  to tetrafluoroethylene (TFE), as shown in Example 5, gives a broad distribution of telomers. See also Chemistry of Organic Fluorine Compounds, 2nd Ed. M. Hudlicky, 1992, p. 420-427). While  $CF_2I_2$  reacts with TFE, the main product is a 1:1 adduct ( $ICF_2CF_2CF_2I$ ) with only small amounts of 1:2 adduct ( $I(CF_2)_5I$ ) and trace of 1:3 adduct ( $I(CF_2)_7I$ ), as shown in Equation (VI) below:



When  $CF_2=CFCl$  is reacted with  $CF_2I_2$ , a mixture of 1:1 and 1:2 adducts is formed, as shown in Equation (VII) below, where  $n=2$ .



Other higher homologs are also formed (e.g.,  $n$  is 3, 4, etc.). In general, higher ratios of olefinic starting materials to  $CF_2I_2$  yield higher telomers (i.e.,  $n$  is higher). The degree of telomerization is limited by product solidification. Preferably, the ratio of olefinic starting material to  $CF_2I_2$  is from about 1:1 to 5:1.

The diiodocompounds formed by the instant process, when one of X, Y, Z or Q is a functional group as represented by  $R_F$  or  $OR_F$ , may be used to chain extend or graft the resulting polymer onto another polymer, or to react to form a specific chain end which may act to change the polymer's surface properties. One example of this would be the production of a potential surfactant material when  $R_F$  is a fluorinated ester or fluorinated sulfonyl group.

Compounds provided by this invention include compounds where each A is  $(CH_2CHR_F)$ . Of note are compounds of this type having the formula

$$40 \quad ICF_2CH_2CHR_FI.$$

In the Examples below, unless otherwise specified, all reagents were used as received from Aldrich Chemical Co., Milwaukee, WI.  $\text{CF}_2\text{I}_2$  was made according to the procedure as described in co-pending U.S. Patent Application No. 60/012,160.

- 5 Gas chromatography (GC) was performed on an HP 5890 II Plus gas chromatograph (Hewlett Packard, Wilmington, DE), using a 20% OV-210 column (Supelco, Bellefonte, PA), with an initial temperature of 50°C, a final temperature of 250°C, and a rate of 15°C/min. The  $^1\text{H}$  and  $^{19}\text{F}$  nuclear magnetic resonance (NMR) data were obtained using a GE Plus NMR spectrometer (General Electric, Schenectady, NY). All measurements are relative to deuterated chloroform ( $\text{CDCl}_3$ ). Ratios given are those for peak areas by GC or molar ratios based on NMR data as designated in the specific examples. High resolution mass spectrometry (HRMS) was done using a Micromass-7070H (VG Analytical, Manchester, UK).
- 10
- 15 The reaction products were obtained by distillation, and their boiling points (bp, °C) were obtained. Elemental analyses were obtained by routine methods.

The following abbreviations are used in the Examples below:

- s = singlet NMR peak
- 20 d = doublet NMR peak
- t = triplet NMR peak
- m = multiplet NMR peak

#### EXAMPLE 1

##### Reaction of $\text{CF}_2\text{I}_2$ with ethylene

- 25 A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 4.0 g of ethylene was added. After the tube was heated at 185°C for 5 hour, 30.3 g of crude product was obtained which was distilled to give 27.3 g of adduct with 100% GC purity, bp 94-95°C/ 50 mmHg.  $^{19}\text{F}$  NMR: -39.1 (t,  $J = 14.3$  Hz);  $^1\text{H}$  NMR: 3.21 (t,  $J = 7.3$  Hz, 2H), 2.95 (m, 2H). HRMS: calcd for  $\text{C}_3\text{H}_4\text{F}_2\text{I}_2$ : 331.8371. Found: 331.8336. Anal: calcd for  $\text{C}_3\text{H}_4\text{F}_2\text{I}_2$ : C, 10.86; H, 1.21; F, 11.45; I, 76, 48. Found: C, 10.84; H, 1.25; F, 11.59; I, 75.96.
- 30

#### EXAMPLE 2

##### Reaction of $\text{CF}_2\text{I}_2$ with propylene

- 35 A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 5.0 g of propylene was added. After the tube was heated at 185°C for 5 hour, 31.6 g of crude product was obtained which was distilled to give 28.7 g of product, bp 106-107°C/ 4.8 mmHg. GC and NMR

indicated a mixture of  $\text{ICF}_2\text{CH}_2\text{CHICH}_3$  and  $\text{ICH}_2\text{CH}(\text{CF}_2\text{I})\text{CF}_3$  in a ratio of 13 to 1.  $^{19}\text{F}$  NMR: for major product: -35.4 (ddd,  $J = 173$  Hz,  $J = 18.4$  Hz,  $J = 8.7$  Hz, 1F), -38.3 (dt,  $J = 173$  Hz,  $J = 16.4$  Hz, 1F).  $^1\text{H}$  NMR: 4.35 (m, 1H), 3.28 (m, 1H), 2.90 (m, 1H), 2.00 (d,  $J = 7.0$  Hz, 3H). HRMS: calcd for  $\text{C}_4\text{H}_7\text{F}_2\text{I}_2$ :

- 5 345.8527. Found: 345.8565 for  $\text{ICF}_2\text{CH}_2\text{CHICH}_3$  and 345.8510 for  $\text{ICH}_2\text{CH}(\text{CF}_2\text{I})\text{CH}_3$ . Anal: calcd for  $\text{C}_4\text{H}_7\text{F}_2\text{I}_2$ : C, 13.89; H, 1.75; F, 10.98; I, 73.38. Found: C, 13.99; H, 1.98; F, 10.80; I, 73.34.

### EXAMPLE 3

#### Reaction of $\text{CF}_2\text{I}_2$ with 4-bromo-3,3,4,4-tetrafluorobutene-1

- 10 A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and 21.0 g of  $\text{BrCF}_2\text{CF}_2\text{CH}=\text{CH}_2$  and cooled to  $-78^\circ\text{C}$ . The tube was evacuated and then heated at  $180^\circ\text{C}$  for 2.5 hour. 31.6 g of crude product was obtained which was washed with aqueous  $\text{Na}_2\text{SO}_3$  solution and distilled to give 28.7 g of  $\text{ICF}_2\text{CH}_2\text{CHICF}_2\text{CF}_2\text{Br}$ , bp  $53^\circ\text{C}/19$  mmHg.  $^{19}\text{F}$  NMR: -36.7 (ddd,  $J = 176.1$  Hz,  $J = 16.2$  Hz,  $J = 7.1$  Hz, 1F), -39.7 (dt,  $J = 176$  Hz,  $J = 15.8$  Hz, 1F), -59.9 (dd,  $J = 178.6$  Hz,  $J = 7.6$  Hz, 1F), -61.0 (dd,  $J = 178.6$  Hz,  $J = 5.6$  Hz, 1F), -94.6 (dt,  $J = 260.6$  Hz,  $J = 7.2$  Hz, 1F), -109.8 (ddd,  $J = 261.0$  Hz,  $J = 18$  Hz,  $J = 7.4$  Hz, 1F).

### EXAMPLE 4

#### Reaction of $\text{CF}_2\text{I}_2$ with 4-iodo-3,3,4,4-tetrafluorobutene-1

- 20 A 75 mL of shaker tube was charged with 42.3 g of 1:1 mixture of  $\text{CF}_2\text{I}_2$  and  $\text{ICF}_2\text{CF}_2\text{CH}=\text{CH}_2$  and cooled to  $-78^\circ\text{C}$ . The tube was evacuated and then heated at  $180^\circ\text{C}$  for 2.5 hour. 36 g of crude product was obtained, which was washed with aqueous  $\text{Na}_2\text{SO}_3$  solution and distilled to give 23.5 g of  $\text{ICF}_2\text{CH}_2\text{CHICF}_2\text{CF}_2\text{I}$ , bp  $118-120^\circ\text{C}/10$  mmHg.  $^{19}\text{F}$  NMR: -36.7 (ddd,  $J = 175.5$  Hz,  $J = 16.0$  Hz,  $J = 7.7$  Hz, 1F), -39.6 (dt,  $J = 175.5$  Hz,  $J = 16.0$  Hz, 1F), -54.8 (ddt,  $J = 202.2$  Hz,  $J = 7.3$  Hz,  $J = 2.3$  Hz, 1F), -56.0 (dd,  $J = 203.0$  Hz,  $J = 7.0$  Hz, 1F), -88.3 (dt,  $J = 261.0$  Hz,  $J = 7.0$  Hz, 1F), -106.2 (ddd,  $J = 261.0$  Hz,  $J = 19$  Hz,  $J = 8.4$  Hz, 1F).

### EXAMPLE 5

#### Reaction of $\text{CF}_2\text{I}_2$ with tetrafluoroethylene

- 30 A 400 mL of shaker tube was charged with 152 g of  $\text{CF}_2\text{I}_2$  and cooled to  $-78^\circ\text{C}$ . After the tube was evacuated and then heated to  $185^\circ\text{C}$ , 20 g of TFE was added and the tube kept at  $185^\circ\text{C}$  for 2 hours. Additional 20 g of TFE was added and the tube was kept for 2 hours. Finally, 10 g of TFE was added and the tube kept for 6 hours. 192.3 g of crude products were obtained and GC indicated that a mixture of 82%  $\text{I}(\text{CF}_2)_3\text{I}$  and 7%  $\text{I}(\text{CF}_2)_5\text{I}$ . Distillation gave 169.6 g of  $\text{I}(\text{CF}_2)_3\text{I}$  with 2.5% of  $\text{I}(\text{CF}_2)_5\text{I}$ , bp  $76-80^\circ\text{C}/150$  mmHg, and 13.1 g of high boiling residue containing 20%  $\text{I}(\text{CF}_2)_3\text{I}$ , 70%  $\text{I}(\text{CF}_2)_5\text{I}$  and 5%  $\text{I}(\text{CF}_2)_7\text{I}$ .  $^{19}\text{F}$  NMR for  $\text{I}(\text{CF}_2)_3\text{I}$ :



-58.2 (t,  $J = 4.7$  Hz, 4F), -105.2 (t,  $J = 4.7$  Hz, 2F); for  $\text{I}(\text{CF}_2)_5\text{I}$ : -59.4 (t,  $J = 4.6$  Hz, 4F), -113.6 (s, 4F), -120.6 (m, 2F).

### EXAMPLE 6

#### Reaction of $\text{CF}_2\text{I}_2$ with trifluoroethylene

- 5 A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 16.0 g of trifluoroethylene was added. After the tube was heated at 185°C for 10 hour, GC indicated 70% of conversion and 26.3 g of crude product was obtained which was washed with aqueous  $\text{Na}_2\text{SO}_3$  solution and distilled to give 1.5 g of 55% pure of adduct, 2.5 g of 84%  
10 pure adduct and 12.8 g of pure product bp 83°C/80 mmHg.  $^{19}\text{F}$  NMR and GC indicated a mixture  $\text{ICF}_2\text{CHFCF}_2\text{I}$  and  $\text{ICF}_2\text{CF}_2\text{CHF}_2\text{I}$  in a ratio of 1.5 to 1.  $^{19}\text{F}$  NMR:  $\text{ICF}_2\text{CHFCF}_2\text{I}$ : -52.6 (dm,  $J = 207.8$  Hz, 2F), -54.8 (dm,  $J = 207.8$  Hz, 2F), -176.2 (m, 1F);  $\text{ICF}_2\text{CF}_2\text{CHF}_2\text{I}$ : -57.9 (dm,  $J = 207.8$  Hz, 1F), -59.8 (dt,  $J = 207.8$  Hz,  $J = 6.5$  Hz, 1F), -101.0 (ddt,  $J = 273.1$  Hz,  $J = 32.3$  Hz,  $J = 6.3$  Hz, 1F),  
15 -116.3 (dm,  $J = 273.1$  Hz, 1F), -165.7 (m, 1F). HRMS: calcd. for  $\text{C}_3\text{HF}_5\text{I}_2$ : 385.8088. Found: 385.8023. Anal: calcd for  $\text{C}_3\text{HF}_5\text{I}_2$ : C, 9.34; H, 0.26; F, 24.62; I, 65.78. Found: C, 9.25; H, 0.27; F, 24.39; I, 65, 81.

### EXAMPLE 7

#### Reaction of $\text{CF}_2\text{I}_2$ with vinylidene fluoride

- 20 A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 10.0 g of  $\text{CF}_2=\text{CH}_2$  was added. After the tube was heated at 185°C for 8 hour, GC indicated 10%  $\text{CF}_2\text{I}_2$  and 79.5% of adduct (area ratio). 35.1 g of crude products were obtained which was distilled to give 4.1 g of 50% pure of adduct and 26.4 g of pure adduct, bp  
25 80-81°C/60 mmHg.  $^{19}\text{F}$  NMR and GC indicated a mixture  $\text{ICF}_2\text{CH}_2\text{CCF}_2\text{I}$  and  $\text{ICF}_2\text{CF}_2\text{CH}_2\text{I}$  in a ratio of 27.6 to 1.  $^{19}\text{F}$  NMR:  $\text{ICF}_2\text{CH}_2\text{CF}_2\text{I}$ : -39.6 (m);  $\text{ICF}_2\text{CF}_2\text{CH}_2\text{I}$ : -59.6 (t,  $J = 4$  Hz, 2F), -101.5 (t,  $J = 16.4$  Hz, 2F). HRMS: Calcd for  $\text{C}_3\text{H}_2\text{F}_4\text{I}_2$ : 367.8182. Found: 367.8168 for  $\text{ICF}_2\text{CH}_2\text{CF}_2\text{I}$ ; 367.8150 for  $\text{ICF}_2\text{CF}_2\text{CH}_2\text{I}$ . Anal: calcd for  $\text{C}_3\text{H}_2\text{F}_4\text{I}_2$ : C, 9.80; H, 0.55; I, 69.00. Found: C,  
30 9.76; H, 0.62; I, 68.48.

### EXAMPLE 8

#### Reaction of $\text{CF}_2\text{I}_2$ with vinyl fluoride

- A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 6.0 g of vinyl fluoride was added. After  
35 the tube was heated at 185°C for 5 hour, GC indicated 90% of conversion and 27.8 g of crude product was obtained which was distilled to give 4.9 g of 55% pure of adduct and 17.1 g of pure product, bp 87-89°C/50 mmHg.  $^{19}\text{F}$  NMR and GC indicated a mixture  $\text{ICF}_2\text{CH}_2\text{CCF}_2\text{HI}$  and  $\text{ICF}_2\text{CF}_2\text{CH}_2\text{HI}$  in a ratio of 8.6 to 1.

$^{19}\text{F}$  NMR:  $\text{ICF}_2\text{CH}_2\text{CHI}$ : -37.6 (dm,  $J = 178.5$  Hz, 1F), -40.33 (dm,  $J = 178.5$  Hz, 1F), -144.7 (m, 1F);  $\text{ICF}_2\text{CFHCH}_2\text{I}$ : -51.8 (ddd,  $J = 195.5$  Hz,  $J = 21.0$  Hz,  $J = 7.4$  Hz, 1F), -56.3 (ddd,  $J = 196$  Hz,  $J = 21.7$  Hz,  $J = 7.3$  Hz, 1F), -176.8 (m, 1F). HRMS: calcd for  $\text{C}_3\text{H}_3\text{F}_3\text{I}_2$ : 349.8280. Found: 349.8391 for  $\text{ICF}_2\text{CH}_2\text{CFHI}$ ; 349.8307 for  $\text{ICF}_2\text{CFHCH}_2\text{I}$ . Anal: calcd for  $\text{C}_3\text{H}_3\text{F}_3\text{I}_2$ : C, 10.30; H, 0.86. Found: C, 10.26; H, 1.00.

#### EXAMPLE 9

##### Reaction of $\text{CF}_2\text{I}_2$ with hexafluoropropylene

A 75 mL of shaker tube was charged with 45.6 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 24.0 g of hexafluoropropylene was added. After the tube was heated at 185°C for 12 hour, GC indicated 55% of conversion and 40.1 g of crude were washed with aqueous  $\text{Na}_2\text{SO}_3$  solution and then distilled to give 6.2 g of 82% pure of  $\text{CF}_2\text{I}_2$ , 2.7 g of a mixture of 60% of  $\text{CF}_2\text{I}_2$  and 28% of  $\text{ICF}_2\text{CF}_2\text{CFICF}_3$ , bp 40-63°C/95 mmHg, 3.0 g of a mixture of 23% of  $\text{CF}_2\text{I}_2$  and 62% of  $\text{ICF}_2\text{CF}_2\text{CFICF}_3$ , bp 64-71°C/95 mmHg and 10.6 g of 93% pure  $\text{ICF}_2\text{CF}_2\text{CFICF}_3$ , bp 74-76°C/95 mmHg. HRMS: calcd for  $\text{C}_4\text{F}_8\text{I}_2$ : 453.7962. Found: 453.7915 for  $\text{ICF}_2\text{CF}_2\text{CFICF}_3$ ; 3452.7967 for  $(\text{ICF}_2)_2\text{CFCF}_3$ .

#### EXAMPLE 10

##### Reaction of $\text{CF}_2\text{I}_2$ with perfluoromethyl vinyl ether

A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 22.0 g of perfluoromethyl vinyl ether was added. After the tube was heated at 185°C for 3.5 hour, GC indicated 76% of conversion and 37.2 g of crude products were distilled to give 13.8 g of 47.6% of  $\text{CF}_2\text{I}_2$  and 46.7% of adduct, bp 50-79°C/100 mmHg and 18.4 g of 99% pure adduct, bp 87-89°C/50 mmHg.  $^{19}\text{F}$  NMR and GC indicated a mixture  $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$  and  $(\text{ICF}_2)_2\text{CFOCF}_3$  in a ratio of 12 to 1.  $^{19}\text{F}$  NMR for  $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$ : -55.0 (dm,  $J = 204.1$  Hz, 1F), -55.3 (d,  $J = 11.3$  Hz, 3F), -58.4 (ddm,  $J = 205$  Hz,  $J = 26.4$  Hz, 1F), -68.0 (m, 1F), -102.6 (dt,  $J = 276.2$  Hz,  $J = 7.7$  Hz, 1F), -104.2 (dt,  $J = 276.4$  Hz,  $J = 7.2$  Hz, 1F); for  $(\text{ICF}_2)_2\text{OFCF}_3$ : -51.7 (m, 3F), -53.9 (m, 4F), -124.2 (m, 1F); HRMS: calcd for  $\text{C}_4\text{F}_8\text{I}_2\text{O}$ : 469.7911. Found: 469.7930 for  $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$ ; 469.7967 for  $(\text{ICF}_2)_2\text{CFOCF}_3$ .

#### EXAMPLE 11

##### Reaction of $\text{CF}_2\text{I}_2$ with perfluoropropyl vinyl ether

A 75 mL of shaker tube was charged with 30.5 g of  $\text{CF}_2\text{I}_2$  and cooled to -78°C. The tube was evacuated and then 60.0 g of perfluoropropyl vinyl ether was added. After the tube was heated at 185°C for 3.5 hour, 78.5 g of crude products were distilled to give 29.0 g of perfluoropropyl vinyl ether; 6.2 g of 72% pure of adduct, bp 30-80°C/40 mmHg; 27.6 g of pure adduct, bp

- 83-84°C/40 mmHg; and 4.4 g of 68% pure adduct, bp 85°C/40 mmHg to 74°C/15 mmHg. Yield 79%. <sup>19</sup>F NMR and GC indicated a mixture ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> and (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> in a ratio of 85.4 to 13.6. <sup>19</sup>F NMR for ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>: -55.3 (d, J = 204.6 Hz, 1F), -58.8 (ddd, J = 204.6 Hz, J = 27 Hz, J = 6.3 Hz, 1F), -68.7 (m, 1F), -81.3 to -81.9 (m, 4F), -90.7 (d, J = 147.6 Hz, 1F), -102.4 (dt, J = 276.7 Hz, J = 8 Hz, 1F), -104.4 (dt, J = 276.6 Hz, J = 7.5 Hz, 1F), -130.4 (s, 2F). (ICF<sub>2</sub>)<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>: -53.8 (m, 4F), -79.4 (m, 2F), -81.3 (M, 3F), -122.3 (m, 1F), -129.3 (M, 2F). HRMS: calcd for C<sub>6</sub>F<sub>12</sub>I<sub>2</sub>O: 569.7847. Found: 442.8824 for ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>-I; 569.7796 for (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>. Anal: calcd for C<sub>6</sub>F<sub>12</sub>I<sub>2</sub>O: C, 12.65; I, 44.55. Found: C, 12.72; I, 44.23.

### EXAMPLE 12

#### Reaction of CF<sub>2</sub>I<sub>2</sub> with CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me

- A 240 mL of shaker tube was charged with 30.5 g of CF<sub>2</sub>I<sub>2</sub> and 60.0 g of CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 3.5 hour. 82.2 g of a mixture of 5% of ICF<sub>2</sub>CF<sub>2</sub>COF, 4% of CF<sub>2</sub>I<sub>2</sub>, 31% of CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me, 9% ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me and 51% adduct were obtained (GC area). Distillation gave 12.3 g of mainly CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me, bp 40-88°C/60 mmHg, 8.6 g of material containing 45% CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me and 55% of ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me, bp 82°C/50 mmHg to 102°C/4 mmHg, and 45.9 g of adduct, bp 103-110°C/3 mmHg. The adduct was a mixture of ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me and (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me.

### EXAMPLE 13

#### Reaction of CF<sub>2</sub>I<sub>2</sub> with CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN

- A 240 mL of shaker tube was charged with 30.5 g of CF<sub>2</sub>I<sub>2</sub> and 45.0 g of CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 4 hour. 67.8 g of crude products were obtained. Distillation gave 15 g of mainly CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN, bp 85-100°C, 37.6 g of adduct, bp 115-116°C/30 mmHg. The adduct was a mixture of ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN and (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN in a ratio of 5.7 to 1. <sup>19</sup>F NMR for ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN: -55.5 (d, J = 205.2 Hz, 1F), -58.9 (ddd, J = 205.5 Hz, J = 27.3 Hz, J = 6.0 Hz, 1F), -69.4 (m, 1F), -79.1 to -80.4 (m, 4F), -84.1 to -85.2 (m, 2F), -90.0 (dm, J = 152.5 Hz, 1F), -102.0 (dm, J = 277.7 Hz, 1F), -104.5 (dm, J = 277.7 Hz, 1F), -108.6 (m, 2F), -145.1 (t, J = 21.2 Hz, 0.5F),

-145.6 (t, J = 21.3. Hz, 0.5F); for (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN: -53.1 (m, 2F), -54.5 (m, 2F), -78.2 (m, 2F), -80.1 (m, 3F), -84.1 (m, 2F), -108.4 (m, 2F), -121.2 (m, 1F), -144.6 (m, 1F). HRMS: Calcd for C<sub>9</sub>F<sub>15</sub>I<sub>2</sub>NO<sub>2</sub>-I, 565.8734. Found: 565.8716 (M<sup>+</sup>-I). Anal: calcd for C<sub>9</sub>F<sub>15</sub>I<sub>2</sub>NO<sub>2</sub>: C, 15.60; N, 2.02; I, 36.63. Found: C, 16.26; N, 2.02; I, 35.74.

#### EXAMPLE 14

##### Reaction of CF<sub>2</sub>I<sub>2</sub> with CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F

A 240 mL of shaker tube was charged with 30.5 g of CF<sub>2</sub>I<sub>2</sub> and 50.0 g of CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and cooled to -78°C. After being  
 10 evacuated at -78°C, the tube was heated at 185°C for 4 hour. 71.3 g of crude products were obtained. Distillation gave 10.3 g of CF<sub>2</sub>I<sub>2</sub>, 42 g of adduct, 95-97°C/5.4 mmHg. The adduct was a mixture of ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F in a ratio of 5.2 to 1. <sup>19</sup>F NMR for  
 15 ICF<sub>2</sub>CF<sub>2</sub>CFIOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F: +45.3 (m, 1F), -55.6 (d, J = 204.7 Hz, 1F), -58.9 (ddd, J = 204.7 Hz, J = 27.2 Hz, J = 6.3 Hz, 1F), -69.3 (m, 1F), -79.3 to -80.2 (m, 4F), -89.8 (dm, J = 144.3 Hz, 1F), -101.9 (dm, J = 277.9 Hz, 1F), -104.6 (dt, J = 277.8 Hz, J = 7.7 Hz, 1F), -112.2 (m, 2F), -145.4 (m, 1F); for (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F: -53.2 (m, 2F), -54.5 (m, 2F), -78.2 (m,  
 20 2F), -80.1 (m, 5F), -112.4 (m, 2F), -121.2 (m, 1F), -144.6 (m, 1F).

#### EXAMPLE 15

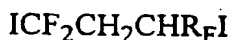
##### Reaction of CF<sub>2</sub>I<sub>2</sub> with

##### CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F at high temperature

A 240 mL of shaker tube was charged with 30.6 g of CF<sub>2</sub>I<sub>2</sub> and 50.0 g of  
 25 CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 4 hour and 240°C for 8 hours. 71.5 g of crude products were obtained. GC indicated a mixture of ICF<sub>2</sub>CF<sub>2</sub>COF, ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F, and (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F in a ratio of 4.1:6.6:1 (area ratio).  
 30 Distillation gave 12.6 of 93% pure ICF<sub>2</sub>CF<sub>2</sub>COF, bp 58-63°C, 6.0 g of a mixture of ICF<sub>2</sub>CF<sub>2</sub>COF and ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F, bp 26-100°C/200 mmHg, 17.9 g of ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F, bp 100-102°C/200 mm Hg, 16.7 g of a mixture of 75% ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 16% (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F and 4.3 g of  
 35 (ICF<sub>2</sub>)<sub>2</sub>CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F. <sup>19</sup>F NMR for ICF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F: + 45.5 (m, 1F), -58.7 (dm, J = 213.7 Hz, 2F), -60.0 (dm, J = 214 Hz, 2F), -76.9 (m, 3F), -77.9 (dd, J = 139.2 Hz, J = 22.7 Hz, 1F), -79.7 (dm, J = 139.2 Hz, 1F), -122.2 (s, 2F), -133.6 (m, 1F).

What is claimed is:

1. A process for making diiodofluorinated compounds of the formula  $\text{ICF}_2(\text{A})_n\text{I}$  wherein  $n$  is an integer of at least 1 and each  $\text{A}$  is  $\text{CXYCQZ}$  wherein each  $\text{X}$ ,  $\text{Y}$ ,  $\text{Q}$ , and  $\text{Z}$  are each independently selected from the group consisting of  $\text{H}$ ,  $\text{F}$ ,  $\text{Cl}$ ,  $\text{R}_\text{F}$  and  $\text{OR}_\text{F}$ , and  $\text{R}_\text{F}$  is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to 20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride, comprising:
  - reacting an olefin of the formula  $\text{CXY}=\text{CQZ}$  with  $\text{CF}_2\text{I}_2$  at a temperature in the range of from about  $120^\circ\text{C}$  to  $240^\circ\text{C}$ .
2. The process of Claim 1 wherein the temperature is between about  $170^\circ\text{C}$  and about  $190^\circ\text{C}$ .
3. The process of Claim 1 wherein  $n$  is 1 to 5.
4. The process of Claim 1 wherein  $n$  is 1 to 3.
5. The process of Claim 1 wherein  $n$  is 1.
6. The process of Claim 1 where  $\text{X}$  and  $\text{Y}$  are each  $\text{F}$ .
7. The process of Claim 6 wherein the olefin is selected from the group consisting of  $\text{CF}_2=\text{CFH}$ ,  $\text{CF}_2=\text{CFCF}_3$  and  $\text{CF}_2=\text{CH}_2$ .
8. The process of Claim 1 wherein the olefin is  $\text{CF}_2=\text{CF}_2$  or  $\text{CF}_2=\text{CFCl}$ .
9. The process of Claim 1 wherein the olefin is a perfluorovinylether of the formula  $\text{CF}_2=\text{CFOR}_\text{F}$ .
10. A diiodofluorinated compound of formula:



- wherein  $\text{R}_\text{F}$  is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to 20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride.

## INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/US 97/08166

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C17/278 C07C17/275 C07C19/16 C07C41/30 C07C43/12  
C07B37/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 926 411 A (PENNSALT CHEMICALS CORPORATION) 15 May 1963 see example 7 ---	1-3,6,7
A	US 2 551 639 A (C.F. FEASLEY ET AL.) 8 May 1951 see claims ---	1
A	J. ORG. CHEM. (JOCEAH,00223263);84; VOL.49 (1); PP.205-7; UNIV. FLORIDA;DEP. CHEM.; GAINESVILLE; 32611; FL; USA (US), XP002039805 ELSHEIMER S ET AL: "Difluorodiodomethane: its preparation, properties and free-radical reactions" cited in the application see the whole document -----	1



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Date of the actual completion of the international search

5 September 1997

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 97/08166

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 926411 A		DE 1274581 B FR 1231263 A GB 926412 A	28-09-60
US 2551639 A	08-05-51	NONE	

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